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Elastomeric Adhesives

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I. INTRODUCTION

At first, there was only natural rubber, a substance "discovered" by Christopher Columbus on his second voyage to the New World. Soft and tacky when solidified from the tree latex, it remained a curiosity for many years, eventually finding use as a "rubber," as Joseph Priestley called it, since it would harden and rub-out pencil markings after it had aged some. The patent literature shows activity after 1791 when the first U.S. patent was issued for a mixture of rubber and solvent that was used to bond two layers of wool fabric together. In 1845, a patent was issued for an adhesive to be used in a self-adhering bandage that contained India Rubber, Gum of Southern Pine, Balsam of Peru, Ground Litharge, Extract of Capsicum Annum, and Turpentine. Just a few years earlier in 1839, Charles Goodyear discovered that the addition to natural rubber of sulfur and certain metallic oxides followed by heating changed the gummy rubber to a stretchable elastic material that, upon release of applied stress, would regain its original shape. Johnson and Johnson developed and patented a pressure sensitive adhesive that contained gum rubber and zinc oxide in 1899.

Also in 1899, Hermann Staudinger graduated from high school in Worms, Germany, continued his studies at several universities, eventually becoming a Professor of Organic Chemistry at the Institute of Chemistry of the Technische Hochschule in Karlsruhe, Germany. In the early 1920s, Professor Staudinger proposed a theory of macromolecular formation. Although his proposals were not immediately widely accepted, a number of researchers pursued certain aspects of his work. And with that research came the foundation of today's synthetic rubber and plastics industries. By the 1930s, a whole host of new, high molecular weight polymers had been developed and were being refined into usable products. In the early to mid-1930s, there was little demand for these new polymers simply because the Southeast Asian natural rubber plantations, which had supplanted the original Brazilian forest collections, supplied all the necessary materials for most elastomeric applications at very low costs. By the late 1930s, that situation had changed, and rather dramatically. War on two continents increased the need for developing sustainable supplies of rubber materials to continue supplying the needs of industry, and eventually, the supplies of the war machines. Japan invaded and took control of Southeast Asia and, with it, the rubber plantations, which immediately threw the rest of the industrial world into disarray. Without natural rubber for tires, gaskets, belting, and hoses, and

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the rubber-based adhesives used to make those products, modern civilization would have come quickly to a halt.

This situation was recognized immediately by the governments of both Germany and the United States, which embarked on the development of replacement supplies through the building of a synthetic rubber industry. In the United States, polychloroprene (Neoprene), styrene-butadiene rubber [General-purpose Rubber—Styrene (GRS), or Buna S], butyl, and acrylonitrile butadiene [General-purpose Rubber—Nitrile (GRN), or Buna N] were the primary polymers pursued for production. By the early 1940s, synthetic rubber production was underway, while the government instituted strict controls over existing supplies of natural rubber, both in solid bale form and latex, since there were some products that still required the use of natural rubber for manufacture. Even old tires, belting, hoses, molded goods, and other rubber fabricated materials were collected as the rubber reclaim industry grew out of the necessity to recover any usable elastomeric polymer. These controls were maintained in place by the U.S. government through the late 1940s and early 1950s, since the rubber plantations did not immediately recover full capacity and distribution immediately after the war. A limited supply of natural rubber allowed the synthetic rubber industry to grow in industrial markets and prosper into the 1950s, as new developments and continued high rates of production reinforced the stability of this new supply of polymers and kept production costs low.

However, despite all of this burgeoning growth of these new materials, natural rubber could not be replaced for all applications. Natural rubber has a molecular weight of approximately 1 million, solution grade styrene-butadiene rubber is typically only 100,000. Natural rubber does not have the natural chemical resistance of nitrile rubber, but can be compounded for many of the same properties, and is more often less expensive to use. While many synthetic elastomers have unique and special properties, natural rubber had the advantage, in the early years after the war especially, of nearly 150 years of experimentation, development, and production. As the century progressed into the 1960s and 1970s, however, Southeast Asia once again became embroiled in war and, even though the primary supplying countries of Malaysia and Indonesia were not directly involved, changes in supplies and distribution assisted the growth and acceptance of many synthetic polymers. As the synthetic rubber industry continued to grow, so did the products become more economical to use.

II. COMMON PROPERTIES OF ELASTOMERIC ADHESIVES

Since natural rubber is the foundation of the rubber industry, all materials that are so-called elastomers, or rubber, are essentially compared against it. Therefore, elastomers are, generally, high molecular weight polymers that elongate or stretch, are crosslinkable, have the unique cured property of rebound or the ability to snap back to an original configuration upon release of stress, have high resilience and compression strength, and have high tensile strength and modulus when stretched. All uncured rubber materials exhibit the characteristic of viscoelasticity, which combines the properties of both solids and liquids, being both stretchable and "liquid-like," or viscous, in the solid state. Rubbery polymers, in addition, also have a high degree of resistance to water in both the uncured and cured states, as well as fairly good resistance to heat and cold when properly compounded and cured. The long chain crosslinked polymers also generally have relatively high tear resistance, are usually quite flexible, and highly resistant to fatigue stress.

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Now, while many rubber polymers exhibit many of these properties, none of them exhibits all of them, nor equally well. Each polymer type has its own unique set of properties and characteristics, which allows for an expanding array of choices for assembly applications. Listed below are the major areas in which elastomeric adhesives provide an advantage over other polymer types.

Fast strength development Whether used as a base for pressure sensitive adhesives or for contact bond adhesives, most rubber polymer-based adhesives exhibit the characteristic of *green strength*, or the ability to virtually instantaneously develop holding power to a surface. Few other polymer systems have this property to as high a degree, or to as wide an array of surfaces and process conditions. This quick bond feature is a great asset to many assembly processes and manufacturing operations.

Versatility Rubber-based adhesives can be compounded to stick to almost anything under almost any conditions. Bond strength can vary from a temporary holding pressure sensitive product, with a few grams per linear centimeter of peel strength, to a high strength structural bond exhibiting hundreds of kilograms per square centimeter of lap shear strength.

Variety Although there are only a few basic categories of rubber polymers that make up the majority of applications, these polymers come in a wide array of distinct product grades within each category. In addition, most of these polymers are compatible with, and can be mixed freely with, other rubbery polymers to provide even more choices of properties, not to mention the virtually endless numbers of fillers, additives, reinforcing and tackifying resins, other polymer types, plasticizers, and other ingredients that can be used to further modify basic properties.

Economy For many applications, rubber-based adhesives and sealants are inexpensive relative to the base cost of many other polymer systems. In addition, the costs for dispensing and application tooling are often low. The speed of assembly operations with quick-stick adhesives often provides a labor and total cost advantage, and may even lower tooling costs.

Flexibility The inherent resilience of rubber polymers often provides protection in expansion/contraction modes due to product temperature cycling and flex stress from repetitive work cycles. Plus this flexibility improves the assembly's resistance to vibration, fatigue, impact, shear, elongation, and peel forces.

Variety of forms Rubber-based adhesives can be supplied to the user in solvent or water-based formulations, as a solid hot melt or a soft tacky extrusion, as a tape (reinforced or not, single or double-sided), as a film, and even pre-applied to a surface for later solvent or heat activation. Products can be single or multiple component, depending on the application requirements.

Variety of bonding methods The numerous forms and types of rubber-based adhesives and sealants also provide for numerous mechanisms for developing bonds to surfaces. Contact bond, pressure sensitive, wet bond, heat reactivation, and solvent reactivation are all feasible modes of product assembly with these products.

Ease of modification Most elastomeric adhesives can be readily modified in viscosity, tack, drying time (for solvent-based products), strength properties, heat resistance, aging characteristics and other properties to fit process and

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user requirements, usually without significant changes to basic characteristics or costs.

Thermoplastic or thermosetting A property often available in the same compound. However, typically, low strength requirements and ambient applications usually are solved with thermoplastic noncuring elastomeric adhesives, while high strength and high heat resistance are obtained from rubber polymers that are crosslinked. Thermoplastic adhesives will often begin losing strength at temperatures above 70°C. Some adhesives actually operate as a thermoplastic until the ambient temperature rises, at which time the adhesive will gain strength through a crosslinking mechanism and function as a thermoset thereafter. There is usually a time limit on the ability of an adhesive to function in this manner, since most curing functions are time–temperature dependent and most of these dual type products will achieve some limited crosslinking at ambient conditions. Some curing mechanisms for elastomers do require exposure to elevated temperatures to effect a suitable cure.

III. CHEMICAL TYPES OF ELASTOMERIC ADHESIVES

Many polymers exhibit some of the characteristics of the elastomeric family. Plastics, both thermoplastic and thermoset types, are very close both in terms of chemical structure and physical properties. Under a given set of conditions, plastics and elastomers will react much the same way. In fact, some polymer types are so versatile as to cross over into several different classes of compounds. The acrylic family is one, with rigid plastic compounds familiar to all in clear glass panel replacement applications, reactive two-component versions that provide a structural thermoset adhesive, rubbery polymers that can be used as sealants or adhesives, and soft thermoplastic polymers that can serve as a starting point for pressure sensitive adhesives or construction sealants, both solvent and water based. The polyurethane family is another, ranging from thermoplastic urethanes (TPUs) used in solid rubber and adhesive applications, to water- and solvent-based formulations, to hot-melt reactive systems for high performance applications where flexibility and green strength is a requirement, to rigid, glassy reactive thermoset polymer systems for structural applications. Other families of polymers that exhibit rubberlike properties include several cellulosic materials, a variety of thermoplastic resins such as acrylonitrile butadiene styrene (ABS) and poly(vinyl chloride) (PVC), and a whole host of vinyl acetate-based compounds. In addition, many silicone compounds and polysulfide systems also fall well into the elastomeric property category. And, obviously, natural rubber possesses these properties. But none of these materials will be described here since most will be covered in detail in other chapters of this treatise concentrating on these particular polymers.

Virtually all rubber materials, and plastic materials, can be made into an adhesive or sealant compound. This is because many elastomers begin as monomers dispersed in water or solvent and are polymerized in situ. Latex products can remain so, while solid elastomers that are extracted from either water or solvent systems can be solvated with an appropriate organic solvent system. In addition, most solid elastomers exhibit thermal flow characteristics which can make them suitable for hot-melt formulations. And since there are many different rubber polymer families, it stands to reason that there will be many different rubber-based adhesives to identify and describe. Some, however, have

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limited usage in the industrial and commercial world, and some have specialty applications because of inherent properties. But for the most part, only a few chemical types make up the majority of rubber-based adhesive and sealant applications. The major rubber families are: Polychloroprene, styrene-butadiene, butyl, and acrylonitrile butadiene. Another class is reclaim rubber, which exhibits many of the properties of the original polymer. The remainder of this chapter will concentrate on providing information on the history, chemistry, forms of use, particular characteristics, and applications of these prime product types.

A. Polychloroprene

At one time, this polymer was one of the most commonly used adhesive types made from a rubber, taking over from natural rubber in the 1950s and 1960s. The primary reason for this high usage was a direct result of the rubber's chemical nature. Structurally, polychloroprene is similar to natural rubber, and in fact was originally described as synthetic natural rubber. The difference between the two is that in the repeat monomer unit that becomes the long chain polymer, polychloroprene has a chlorine atom positioned in one of the positions where natural rubber has a hydrogen atom. This chlorine atom provides the advantage of higher polarity for the polymer molecule, which is a great aid in developing adhesion to a diverse group of surfaces.

Polychloroprene was developed almost by accident. Experimenting with a copper chloride catalyst and acetylene gas in the 1920s, one of the trials by Father Julius Nieuwland of the University of Notre Dame yielded a black tarry substance. Eventually, Dr. Nieuwland was able to synthesize a divinylacetylene polymer and reported his results in a paper. Later, working with DuPont scientists after contact was established following the paper's publication, the reaction conditions were controlled and treatment with hydrochloric acid yielded a chloroprene monomer. Polymerization of that monomer produced a rubberlike polymer that was eventually commercialized as DuPrene, later renamed Neoprene. This new polymer exhibited many of the characteristics of natural rubber in processing, and a number of superior properties in use. Higher chemical resistance, better aging, and improved temperature resistance were just a few properties that were promising. However, since polychloroprene was a manufactured product, it was not competitive with an agricultural product in the 1930s. In addition, for most adhesive applications, higher cost aromatic solvents were required, in part, for dissolution as compared to aliphatic solvents typically used for natural rubber. And in many applications, higher solids contents were required to achieve certain viscosities as compared to natural rubber compounds, which also increased overall cost. During World War II, however, there was high demand for a rubber that matched many of the properties of natural rubber. After the war, polychloroprene retained its popularity because of its exceptional performance in contact bond applications.

Polychloroprene comes in two varieties for manufacturing adhesives: solid rubber, and emulsion or latex. Solid rubber was the preferred form for most of the second half of the twentieth century since it was available in a number of grades, all of which could be intermingled for specific characteristics, and could easily be converted into a solvent-based cement. Most solvents were inexpensive before the oil crisis of the late 1970s, which provided for inexpensive adhesives. Drying times could be controlled with mixtures of solvents, which also allowed for quick process times compared to other adhesive systems. Combination with phenolic resins and metallic oxides yielded improved characteristics that made the compound suitable for myriad applications. However, owing to increasingly

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stringent environmental laws and regulations, solvent-based polychloroprene adhesives have been losing favor in some applications, even though processing and end use performance are usually superior to that of most water-based polychloroprene systems.

1. *Properties*

While there are significant differences between grades of polychloroprene elastomers due to molecular weight differences and crystallinity characteristics, by and large, processing and performance properties may include:

Superior green strength Applying a thin coat of either water-based or solvent-based adhesive onto each of the substrates to be bonded, drying to a tacky-to-the-touch condition, and mating the surfaces with moderate pressure provides excellent contact bond strength. Often this early strength enables immediate processing in the next part of the assembly, or packaging for shipment.

High ultimate strength Although polychloroprene elastomers can be processed as pressure sensitive adhesives, which are typically low strength applications, typical usage is for high strength requirements. On some surfaces, with a reacted phenolic resin as a formula ingredient, a lap shear strength in excess of 70 kg/cm^2 can be achieved.

Wide surface compatibility The high polarity of the base elastomer aids in developing adhesion to virtually all high polarity surfaces. Solvent-based products often develop good adhesion to low polarity surfaces such as polyolefins and other plastic substrates.

Thermoplastic or thermosetting While many contact bond applications require no curing process because an extra strength requirement is not present, in certain formulations polychloroprene will provide ambient cure for improved properties, and can be cured by several different mechanisms for high performance properties. Ambient cure systems are typically one component, while high performance formulations are often two-part systems, or one-component systems cured in elevated temperature conditions.

Resistance to moisture, chemicals, and oils Service conditions and assembly configuration often play a part in total resistance to end use environment, but polychloroprene exhibits excellent performance for most conditions. Constant immersion in any of these materials is not recommended.

Resistance to temperature Depending on the degree of cure, if required, polychloroprenes will typically provide temperature resistance in the $-50^{\circ}C$ to $150^{\circ}C$ range, with special formulations capable of even wider ranges.

Resistance to aging While compounding for outdoor exposure is recommended to provide superior performance, the presence of the chlorine atom in the molecule helps provide better resistance to aging than most synthetic elastomers.

2. *End Uses*

As previously noted, the primary use for this elastomer has been as solvent-based adhesives and sealants. Solvent-based products are losing market share to water-based polychloroprenes, to other polymer types such as acrylics and polyurethanes, and to hot melt adhesives. However, where the processing facility is able to contain the vapor emissions, a solvent-based adhesive or sealant is preferred because of better wetting of surfaces, faster drying, and higher performance of the cured or dried product. Many rubber bonding

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applications for hose and belt manufacture, and for rubber membrane roofing, still recommend a solvent-based product. For applications where high strength is not as big a factor, such as foam fabricating, latex compounds are preferred, sometimes using a two-part system with an acid catalyst to speed processing and bond development. Many leather goods markets, such as belts and shoes, prefer polychloroprene contact bond adhesives because of the fast processing cycles. Polychloroprene adhesives are used to manufacture recreational vehicles, kitchen counter tops, office furniture and partitions, truck and trailer bodies, plastic and composite wood bonding, gasket and trim bonding, floor tile mastics, and many other applications. These polymers can be converted into heat and solvent reactivatible films.

B. Butyl Rubber

Building on technologies first developed in Germany in the early 1930s, Robert M. Thomas and William J. Sparks, both employees of Standard Oil (now ExxonMobil Chemical), patented a new synthetic rubber in 1937. Butyl rubber is characterized by a very saturated linear polymer chain, leaving little space between molecules for transmission of air, vapors, moisture, or water. As such, butyl rubber was successfully used during World War II as a substitute for natural rubber in the manufacture of tire inner tubes and curing bladders.

Butyl rubber is a polymerization product of reacting isobutylene with a portion of an isoprene molecule, thus providing a controlled degree of unsaturation in the resulting polymer chain. The lower the percentage of unsaturation, the more thermoplastic the polymer is; the higher the unsaturation, the more opportunity for crosslinking the polymer into an elastic thermoset. (Unsaturation is a term used to describe the density of carbon–carbon double bonds, i.e., reactive sites.) The level of unsaturation can be polymerized into the base polymer for specific properties. For some applications, the polymer can be halogenated to increase molecular polarity and functionality, increasing the ability of the polymer to bond to polar surfaces or provide for curing by alternative mechanisms. In addition, partially or pre-crosslinked grades of butyl rubber are available which exhibit higher modulus than base grades. Butyl rubber can be blended with many other elastomers and polymers to modify its basic properties, or the properties of the other elastomer formulation, and the polymer is compatible with many kinds of fillers and additives.

Early adhesive uses of butyl rubber generally consisted of solvent-based dispersions, or tape and "rope" extrusion of formulated solid rubber. Extensive use was made of butyl rubber's inherent tackiness in highly saturated grades of the polymer to make pressure sensitive tapes and precoated films. The polymers are also extensively used as major components of hot-melt adhesives, solid rubber sealing tapes, and caulking grades of sealants and mastics, of which most were high solids content solvent-based formulations.

1. *Properties*

The wide variety of grades available provides for an extremely diverse array of properties that can be developed for butyl rubber adhesives and sealants. However, the following general properties apply to varying degrees.

Superior water and moisture resistance The saturated polymer chain resists passage of water molecules through the chain structure.

Superior resistance to air and gas permeability Also a result of the saturated polymer chain.

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High initial tack Even without tackifying resin, the inherent tack of certain grades provides for excellent contact bond and pressure sensitive adhesives.

Good chemical resistance While not as good as polychloroprene-based products, butyl polymers have resistance to vegetable and animal oils, and many other chemicals. Most solvent and petroleum products will cause swelling, even in cured products.

Wide substrate range Even though the base polymers are of relatively low polarity, the inherent tackiness and linear molecules make them bond to most surfaces. Some compounds are suitable for bonding to polyolefins and other highly unsaturated polymers. However, bond strength for most pressure sensitive applications tends to be quite low, leading to creep under sustained stress. Even crosslinked polymers are often limited to low strength applications.

High flexibility and impact resistance Low levels of crosslinking and subsequent chain entanglements provide for stretching and stress absorption.

Variable heat resistance A wide range of heat resistance is available, usually dependent on the degree of unsaturation in the base polymer and the type of cure mechanism used, if any.

Superior aging performance With few sites for oxidation to take place, butyl rubber compounds are typically very resistant to ambient aging, which accounts for its high volume use in sealant compounds.

Wide range of choices Because butyl rubber comes in so many grades and polymer variations, many kinds of compounds can be formulated. Different curing mechanisms can be used, high levels of fillers can be used, and products can range from very soft to hard.

2. *End Uses*

While popular for many years as solvent-based pressure sensitive adhesives and sealant grade compounds, butyl rubber products have been losing favor to water-based acrylics in recent years. Adhesion performance of the thermoplastic acrylics is often quite similar, and even though drying time is longer for water based versus solvent based, many uses have moved to the acrylics. There are, however, many areas where butyl rubber compounds excel, particularly where water resistance and low permeability are required. Specialty adhesive tapes for pipe wrap, surgical tapes, electrical tapes, and similar areas still often use a butyl rubber base. High solids content butyl rubber sealants are quite popular for many construction and repair operations. Hot melt butyls, either as a straight formulation or compounded with other polymers, are used for carton closing, insulated window sealing, appliance manufacture, and prefabricated metal buildings. Extruded tapes come in several grades and are extensively used for auto glass repair, mobile home and recreational vehicle manufacture, rubber roof installation, and marine applications.

Self-curing solvent-based butyl rubber adhesives are used in bonding ethylene-propene diene monomer (EPDM) rubber to itself in rubber roof seaming, laminating polyethylene film, and as a flocking adhesive for bonding short fibers to surfaces, as in auto window inner seals. Butyl rubber adhesives are also used for a variety of applications in belt and hose manufacture and repair. Water-based butyl rubber adhesives are not as popular as the solvent-based grades, but often are used in pressure sensitive adhesives for paper and foil laminating, and for packaging and laminating applications for many other substrates.

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C. Nitrile Rubber

First made commercially available in Germany in 1936, this elastomer is officially known as acrylonitrile butadiene, and is usually the product of an emulsion polymerization process that combines the two monomers: acrylonitrile and butadiene. However, the polymer can also be made in a solution process, and with a variety of monomers. As a specialty polymer, and even though several commercial brands were available, Buna N (as it was first known) was little used until World War II, when the polymer's unique oil and plasticizer resistance and high heat resistance became very important for transportation products. Nitrile rubber also exhibits exceptional adhesion to metallic surfaces and is compatible with a wide range of additives and compounding ingredients.

Nitrile polymers used for the manufacture of adhesives generally contain 25% or more acrylonitrile, but in the base polymer the acrylonitrile content can vary from 15% to 50%. Increasing the acrylonitrile content improves the oil and plasticizer resistance and increases the polarity of the compound. However, higher levels of acrylonitrile also increase the hardness and modulus of the polymer, reducing the elasticity of the resulting polymer. Nitrile rubber can be produced by a "cold" (5°C) or "hot" (25–50°C) process, with most adhesive polymers produced by the hot process which induces more chain branching. Nitriles can be combined with other monomers in solution polymerization which increases functionality and improves compatibility with other reactive resins like acrylics, epoxies, and polyurethanes.

For many years following World War II, the primary use for nitrile rubber adhesives was as solvent dispersed compounds, often modified with phenolic resin to increase heat resistance and improve strength properties. Water-based nitrile adhesives have been growing in recent years, but do not match the film strength of the solvent-based compounds. Liquid nitriles, particularly carboxy terminated types, have become a popular reactive resin for flexibilizing rigid polymer systems such as epoxies. Nitrile adhesive coated surfaces can be heat or solvent reactivated within a specified time frame, or before cure occurs. Adhesives can be converted to reinforced or nonreinforced films, usually by casting a solvent-based solution onto release paper, for die cutting to part configuration. After part placement, adhesives can be reactivated and cured.

1. *Properties*

Once again, the wide variety of grades and copolymers available in this polymer make generalizations somewhat difficult, except for the following select properties that are inherent to the polymer.

Superior resistance to oils Nitrile rubber has the highest resistance of any of the generally used elastomers to grease, oil, plasticizers, and most organic solvents, both aliphatic and aromatic. There is limited resistance to some polar solvents, and polymers are generally soluble in ketones.

Excellent high temperature resistance When properly cured at elevated temperatures, nitrile adhesives can withstand temperatures above 150°C, with some compounds capable of limited exposure to temperatures above 200°C.

High strength Lap shear can exceed 200 kg/cm^2 on certain substrates, such as some metals, particularly if combined with other reactive resins, such as phenolic or epoxy.

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Good aging Generally requires the addition of antioxidants and ultraviolet (UV) absorbers if exposed for a long term to weathering, but the elastomer has good retention of properties in normal use.

Low building tack Even though used as a contact adhesive for many applications, the adhesive must be freshened with solvent before mating to assure good wet-out; otherwise high contact pressure or the addition of tackifying resins to the formula is required.

Curable Nitrile rubbers can be cured with sulfur or isocyanates, but some formulations exhibit improved properties on elevated temperature cycling, even without curatives. For consistent high performance, the polymer must be cured at elevated temperatures.

Chemical and moisture resistance Like most elastomers, there is a high degree of moisture resistance, and chemical resistance is excellent.

Good processing characteristics Adhesives can be supplied as contact bonding types—either in water- or solvent-based systems—hot-melt, pressure sensitive, or as reactive systems—either 100% solids content or solvent based.

Adhesion properties Exhibits strong bonds to most highly polar surfaces such as metals, but does not bond well to inert surfaces such as polyolefins.

2. *End Uses*

General purpose solvent-based nitrile adhesives are frequently used when resistance to oils and plasticizers is required. Gaskets made from cork, rubber, metal, fiber, and composite blends are often bonded in place with nitrile adhesive. Bonding highly plasticized PVC films to other surfaces and to themselves often requires the superior plasticizer resistance of nitriles, although staining may be a problem with certain combinations of plasticizer and elastomer additives. Nitrile phenolic adhesives have been used for many years for automotive brake and clutch assemblies, for belt and hose manufacture, plastic component assembly, and shoe sole attachment for certain types of outsole materials to leather. In addition, these adhesives have been used for bonding printed circuit wiring boards. Water-based versions are used for laminating vinyl films, and nitrile rubber to fabric and metallic foils. Cast films have been used for bonding honeycomb structures for aircraft assembly, but these films work well for almost any metallic structure.

D. Styrene-Butadiene Rubber

Buna S (as it was first known) was developed in the late 1930s in Germany as a synthetic natural rubber. When the United States needed a synthetic polymer as a replacement for natural rubber as part of the war effort in the early 1940s, chemists at several rubber companies were familiar with that technology and tried to duplicate it. Attempts at developing an emulsion polymerization process failed until Waldo Semon of BF Goodrich consulted with Victor Mills of Procter & Gamble. Ivory soap (99 and 44/100ths pure!) was being used as an emulsifier for the process and it was determined that the small amount of perfume in the soap (part of the other 56/100ths) was a catalyst contaminant. Once the perfume was removed from the soap, the polymerization process was successfully developed, and styrene-butadiene rubber (SBR), which was then called GRS (General-purpose Rubber — Styrene), became the fastest growing of all synthetic rubbers because of its similarity to natural rubber in processing and performance after cure. More than 50

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synthetic rubber plants were built by industry during the war period, under the auspices of the federal government, with the most volume allocated to SBR.

While quite similar to natural rubber, there were differences which prevented really high growth for this copolymer after the war. The molecular weight of SBR from those original processes was only about 100,000 compared to over 1 million for natural rubber. Further, differences in tensile strength, cohesive strength, elongation, hot tear strength, aging, and other properties existed which permitted natural rubber to regain most of its earlier market share. The low cost of SBR, however, made it an excellent blending elastomer. Modifications to the base polymers and continued work with compounding, processing and curing conditions improved the performance of these copolymers. New polymerization processes by the 1950s began to improve many of the original polymer properties in comparison to natural rubber.

Standard SBR materials are made from an emulsion polymerization process and are available in more than 100 grades, but only a few are used as a base for adhesives. The two basic processes for producing these many grades can be either a "hot" or "cold" process, depending on the polymerization temperature, with hot polymerization being the preferred process. Hot polymerized SBR typically yields a lower molecular weight polymer, but with a wider molecular weight distribution which provides for a more balanced polymer. The styrene content can also be varied to enhance certain properties. Emulsion process polymers are often called "random" SBR because there is no control of the attachment sites for the styrene monomer when polymerized. These polymers are often blended with other polymers to lower cost and increase compatibility with various resins, plasticizers, and fillers.

In the mid-1960s, a new form of SBR was introduced called a "block" copolymer. Produced by a solution polymerization process, this material exhibited an ordered molecular structure with the styrene monomer located at the ends of the butadiene monomer chain. In addition, other monomers such as isoprene, ethylene, butylene, and others, could be added to the polymer chain, which further modified basic properties. These materials possess a continuous rubber phase for resilience and toughness, and a discontinuous plastic phase for solubility and thermoplasticity. A variety of different grades are also available for this type of SBR, with differences in molecular weight, differences in the types of monomers used, differences in structural configuration, and differences in the ratio of endblock to midblock. Both emulsion and solution polymerized grades of SBR are available as solvent-based and water-based adhesives and sealants. Block copolymers are extensively used for hot melt formulations and both water-based and solvent-based pressure sensitive adhesive applications. Today, SBR elastomers are the most popular elastomers used for the manufacture of adhesives and sealants.

1. *Properties*

The differences between emulsion and solution polymerized SBRs are significant, although they do share the following similarities.

Superior water and moisture resistance While not recommended for immersion applications, and not as resistant as butyl compounds, these polymers are not affected by most aqueous chemicals.

Ease of dispersion Both emulsion and solution grade polymers are easily dispersed in aliphatic and aromatic solvents and solvent blends, and provide low viscosity, high solids content formulations, with low mixing costs. However, the

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opposite side of this feature is a poor resistance to organic solvents and oils, even when vulcanized.

Good heat resistance Emulsion grade polymers are equal to or better than natural rubber, while block copolymers are superior to natural rubber and emulsion grade SBRs. Block copolymers also are often superior for resistance to cold temperatures.

Low building tack An inherent characteristic of SBR elastomers, which normally requires the addition of tackifying resins, low molecular weight polymers, or plasticizers, or master batch processing.

Excellent substrate compatibility Properly compounded adhesives, sealants, and pressure sensitive materials will adhere to almost any surface. Block copolymers have exhibited superior pressure sensitive adhesion to polyolefin and other low energy surfaces.

Fair to good aging Cured products often will outperform natural rubber products, but uncured products made from emulsion polymers can degrade rather quickly if not compounded for UV, ozone, and oxygen resistance. Block copolymers are typically better in the uncured state than standard SBR, but still require protectant additives for extended exposure conditions.

Good processing characteristics Adhesives are often used as a contact bond type—either in water- or solvent-based systems—as a hot melt, or as a pressure sensitive, in curing systems, or as heat or solvent reactivatible systems. Block copolymers provide superior pressure sensitive adhesives, but can also be compounded for contact bond adhesive or sealant applications.

Curability Typically, these are sulfur cured at elevated temperatures, but can be cured by other mechanisms for higher heat resistance and better strength and aging properties.

Low cost Emulsion polymers are low cost compared to most other synthetic elastomers. Also they can be compounded with a variety of low cost fillers for sealant and low bond strength applications.

2. *End Uses*

The major use for block copolymers is in hot melt and solvent-based pressure sensitive adhesives. These pressure sensitive adhesives are most often used for tapes, and to a lesser degree, for labels. Solids contents of the solvent-based pressure sensitive adhesives are typically in the 40–60% range and are applied by a variety of converting processes, including roll coating, knife coating, and other similar processes. Block copolymers compounded as pressure sensitive adhesives are particularly effective on polyolefin foams, films, and laminates. These products are used in construction applications, automotive padding and insulation, orthopedic devices, packaging, and bookbinding.

Emulsion polymers are typically used in solvent- and water-based formulations, in both curing and noncuring applications. Many applications are similar to those listed for natural rubber applications, being used for bonding paper, fabric, wood, plastic, and other surfaces, often in spray grade formulations. Sulfur curable cements are used in laminating layers of fabric and rubber together for hose, belting, and tire fabrication. Carpets use a major quantity of SBR latex as a binder for backing materials. Emulsions also find extensive use as a binder for nonwoven goods, and in diapers and other personal disposables.

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The construction industry uses several kinds of SBR polymers, in both solvent- and water-based compounds. Ceramic and tile bonding for floors and walls is one area, while solvent-based products for subfloor attachment to joists and panels to studs in building construction is a major area.

E. Other Elastomers

As was noted earlier, virtually any elastomeric material can be, and probably is currently, made into an adhesive or sealant. All elastomers are soluble in one or more organic solvents which allows the production of a solvent-based adhesive. Many elastomers are polymerized in an emulsion process, which yields a latex. And a number of elastomers have a low enough glass transition temperature to permit use as a hot-melt polymer, or as one ingredient in a hot melt formulation. Summary statements describing a few of these other polymers follow, but without the detail provided for the primary elastomers.

1. *Reclaim Rubber*

Even before World War II, reclaim rubber was a popular material for many adhesive and sealant applications. At that time, virtually all rubber was natural rubber, which allowed material that had been de-vulcanized to be processed simultaneously with and to extend the new raw materials. Reclaim rubber has the advantage of already containing a selection of oils, fillers, resins, antioxidants, and antiozonants in the original formulation. When delivered in bale or sheeted form, the reclaim rubber will mix and process much the same as original forms of natural rubber. Since the war, however, and particularly since 1970, reclaim rubber has been losing ground in favor of other polymers. Several factors are contributing to this decline, the first of which is polymer purity. As mentioned, when all rubber was natural rubber, it was easy to find different grades of the same polymer for certain applications and use the reclaim in similar operations. The grades included belting regrind, tire regrind, even baby bottle nipple regrind, among others. Today, however, polymers of all different elastomeric bases enter the processing stream and it is extremely difficult, if not impossible, to separate different synthetic polymers in a blend. Coupled with this is the fact that different manufacturers will use different polymer blends for identical applications.

A second major factor contributing to the decline of reclaim rubber adhesives is the fact that factories processing cured rubber materials for reclaim emit strong odors, particularly sulfurous odors. Many reclaim factories discontinued operations as air emissions rules and regulations became more stringent rather than try to contain the odors with different air control devices, which were both expensive to purchase and expensive to operate. A third major factor contributing to the decline of reclaim rubber is the fact that the highest usage of product made for adhesives and sealants was as a solvent-based product. After passage in 1990 of the Clean Air Act, solvent-based products started to decline in total volume for general industrial applications. This decline was accelerated by the difficulty in obtaining suitable reclaim rubber for specific formulations, since many adhesive formulations get "locked" into specific materials from specific sources. The final factor contributing to the decline in use of reclaim rubber adhesives is that most compounds today are black in color (except for baby bottle nipple regrind), whereas in the past a variety of colors were available.

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Notwithstanding the factors just mentioned, reclaim rubber still remains a part of the elastomeric adhesive supply chain. Adhesives and sealants made from reclaim rubber are inexpensive, compared to a formulation prepared from new raw materials. Reclaim polymers are very compatible with other elastomers, and often improve overall properties when added to certain formulations. Reclaim elastomers can be processed and cured the same as new polymer, but because of the considerable processing used to produce reclaim rubber, when dispersed in solvents, often provide superior spray and substrate wetting properties. Also of value is that the typical reclaim rubber has improved heat resistance. Reclaim rubber is also very compatible with asphalt; blends of these materials are finding extensive use in construction applications. A new and growing application for reclaim polymers is as an ingredient in high performance polymer mixtures such as epoxies and acrylics. The addition of limited amounts of powdered reclaim rubber serves as a "toughening" polymer, providing a degree of elasticity, resilience, and compression strength to rigid polymers.

In addition to widespread use as a blend in asphalt/rubber sealants for roofing and other construction applications, reclaim rubber adhesives have been used as an insulation adhesive, as a pipe wrap adhesive, and as an ingredient in some pressure sensitive adhesives. Of interest is the fact that virtually every telephone installation in the United States before 1985 that required a cable splice used a reclaim rubber adhesive.

2. *Fluoropolymers*

A small, but ultimately very important, part of the elastomer-based adhesive and sealant market is devoted to fluoropolymers. Most often processed as a solvent-based fluorocarbon rubber mixture, these products are often used as sealants for applications requiring a high degree of chemical resistance, particularly where temperatures may rise above 210°C. These polymers exhibit excellent retention of elastomeric and mechanical properties at elevated temperatures, with some products capable of intermittent exposure to temperatures above 315°C. Another application is as a laminating adhesive for polyimide films for electronic components and flexible circuitry. Fluoropolymer sealants and adhesives are also used for bonding gaskets and seals in high performance aircraft and aerospace vehicles, and in a limited way in high performance automotive applications. Some forms of these products also are listed as fluorosilicones. Some curing grades of fluoropolymers are used as a splice cement in the fabrication of rubber fuel cells, in bonding and sealing tank linings, and in other rubber assemblies made of different grades of fluoropolymer.

3. *Polyisoprene*

A true synthetic natural rubber was introduced in the mid-1960s with the exact same chemical structure as latex tapped from a tree. The difference is that natural rubber comes with a variety of other ingredients in the latex that can both add and detract from performance, while polyisoprene is considered relatively "pure." In addition, there are some differences in molecular weight distribution that impact performance. Available in both latex and solid forms, this elastomer can be directly substituted for natural rubber in many applications. Adhesives which are not cured tend to have higher creep values than natural rubber, but also exhibit lower tack and green strength properties. Vulcanized adhesive products perform equal to cured natural rubber adhesive products.

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4. *Ethylene-Propylene Diene Monomer (EPDM)*

EPDM was also introduced in the 1960s. This is a relatively saturated polymer structure with a diene, or double bond carbon monomer, added to provide functionality to the polymer chain. EPDM performs in many respects like butyl rubber in that it has excellent resistance to ozone and oxygen degradation, and has superior UV and weathering resistance. A major difference with butyl polymers is a lower resistance to moisture vapor transmission. The most common use of EPDM is as a sealant for single ply rubber roofing systems, which are themselves made of EPDM rubber. EPDM is available in both emulsion and solid forms, both of which can be easily blended with other elastomers in a formulation. There is also a liquid polymer available for blending and mixing into formulations.

IV. MARKET VALUATION

There are numerous market studies of the adhesive and sealant industry. Some even evaluate subsections of the marketplace, covering, for example, only pressure sensitive products and/or applications, only structural or high performance materials, major end use markets such as packaging or construction, and the raw materials used in making adhesives and sealants. For the most part, none of the studies agree with each other, either in terms of the size of the market, or in the value of individual segments or individual materials. The reasons for this disagreement are typically related to the conduct and parameters of each study, since each research group tends to focus their study a certain way or on a certain segment. In addition, some market segments may even be unknown to some researchers because of so few participants in a tightly defined end user niche. As a consequence, each market study of adhesives and sealants must be gauged on its own merits rather than compared with other studies.

Even so, it is valuable to understand the relative position of individual products in the overall structure of the adhesive and sealant market. Table 1 below provides a good breakdown of elastomeric products in comparison with other major product types. Only the market value of these products is shown, even though most studies, including the one referenced here, include volume data as well. More complete analysis is available from Impact Marketing Consultants, Manchester Center, VT, publisher of the *2000–2002 Rauch Guide to the US Adhesives & Sealants Industry* (see Chap. 2 on Information Resources).

V. CONCLUSIONS

Elastomeric adhesives are formulated from one or more of the many synthetic rubber polymers (or natural rubber) to provide highly flexible, resilient bonds to a variety of substrates. These compounds are based on several basic polymer types and are available in a wide selection of forms for processing by a variety of assembly methods. The most popular synthetic polymer types are: Polychloroprene, styrene-butadiene rubber, nitrile rubber, and butyl rubber. Generally, elastomeric adhesives are characterized by being: Versatile, economical to use, good for quick assembly, available in many standard formulations, easily tailored to process and product requirements, of high peel strength, and thermoplastic or thermosetting.

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Table 1 U.S. Consumption of Adhesives and Sealants in 1998

Chemical type	$ (Million)
Elastomers:	
SBR and block copolymers	581
Polychloroprene	150
Butyl rubber	220
Nitrile rubber	77
Reclaim rubber	44
Other elastomerics	30
Total elastomerics	1102
Natural rubber	350
Epoxy	629
Silicone	860
Phenolic	1650
Polyolefins, including ethylene vinyl acetate (EVA) and vinyl acetate ethylene (VAE)	1290
Polyurethane	960
Acrylics	709
Starch and Dextrin	730
Poly(vinyl acetate)	662
All other types	2908
Total market	11,850

Source: Impact Marketing Consultants.
Given economic conditions since 1998, it is likely that the numbers in this table are relatively consistent with the market value of adhesives in 2002.

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